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1. REPORT DATE (DD-MM-YYYY) 04-10-2004	2. REPORT TYPE REPRINT	3. DATES COVERED (From - To)

4. TITLE AND SUBTITLE RAMAN SCATTERING BY GROUND-STATE ATOMIC OXYGEN	5a. CONTRACT NUMBER
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER 62601F
6. AUTHOR(S) R. D. Sharma	5d. PROJECT NUMBER 1010
	5e. TASK NUMBER BD
	5f. WORK UNIT NUMBER A1

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Air Force Research Laboratory 29 Randolph Road Hanscom AFB MA 01731-3010	8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S) AFRL/VSBYB
	11. SPONSOR/MONITOR'S REPORT NUMBER(S) AFRL-VS-HA-TR-2004-1155

12. DISTRIBUTION / AVAILABILITY STATEMENT
Approved for Public Release; Distribution Unlimited

14. ABSTRACT

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15. SUBJECT TERMS
Atomic oxygen   Raman transitions   Raman LIDAR
Thermodynamic equilibrium   Atmospheric temperature

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON R. D. Sharma
a. REPORT UNCLAS	b. ABSTRACT UNCLAS	c. THIS PAGE UNCLAS	SAR	6	19b. TELEPHONE NUMBER (include area code) 781-377-4198

20041014 003

Raman scattering by ground-state atomic oxygen

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[1] Differential cross sections for Raman scattering between the multiplet levels of the ground electronic state of atomic oxygen are calculated from first principles. The calculated cross sections are in order-of-magnitude agreement with the available experimental measurements. The use of a Raman LIDAR (Light Detection and Ranging) has the potential of giving a three-dimensional map of the density of each of the three fine structure levels of atomic oxygen. Since it was established earlier that the fine structure levels are in local thermodynamic equilibrium (LTE) up to at least 350 km altitude, the Raman LIDAR therefore also has the potential of giving a three-dimensional map of the temperature of the atmosphere. *INDEX TERMS:* 0310 Atmospheric Composition and Structure: Airglow and aurora; 0355 Atmospheric Composition and Structure: Thermosphere—composition and chemistry; 0340 Atmospheric Composition and Structure: Middle atmosphere—composition and chemistry; 0342 Atmospheric Composition and Structure: Middle atmosphere—energy deposition; *KEYWORDS:* atomic oxygen, Raman transitions between fine structure levels, Raman LIDAR, local thermodynamic equilibrium, three-dimensional map of atmospheric temperature and atomic oxygen density

1. Introduction

[2] The role of atomic oxygen in the heat budget of the terrestrial thermosphere can hardly be overestimated [*Sharma and Roble*, 2002]. Three important processes involving atomic oxygen, namely the 15 μm emission pumped by the impacts of O with CO_2, 5.3 μm emission pumped by the impacts of O with NO, and 63 μm fine-structure emission $O(^3P_1) \rightarrow O(^3P_2)$ are the dominant mechanisms for cooling the thermosphere and determining its temperature and density structure [*Sharma and Roble*, 2001]. It is therefore very desirable to know the temperature and density of atomic oxygen in the thermosphere. Recent satellite-based passive remote sensing of atomic oxygen density in the 130–175 km altitude range by measuring the 63 μm limb emission by Cryogenic Infrared Spectrometers and Telescopes for the Atmosphere (CRISTA) aboard ASTRO-SPAS (Astronomical Shuttle Pallet Satellite) for the November 1994 to August 1997 period [*Grossmann et al.*, 2000] have given very surprising results: "The resultant densities are on the average about 40% below the predictions of the MSIS model for the low solar activity conditions of the CRISTA experiments and at all altitudes covered by the measurement. The densities exhibit considerable horizontal structures which are only in partial agreement with the MSIS predicted variations. The latitudinal distribution shows steeper decreases towards the poles than given in MSIS."

[3] The CRISTA measurements, while showing considerable horizontal structure, also, because they are limb measurements, average the structure over the line-of-sight and partially mask it. Since it is possible to gate the scattered Raman pulse, one can determine the O density and temperature in a particular space-time interval, giving us a method of determining these two very important parameters for atmospheric modeling without limb averaging over a couple of thousand kilometers. It is hoped that this work will be as useful to future experiments as our previous work [*Sharma et al.*, 1988, 1990, 1994; *Zachor and Sharma*, 1989] was to CRISTA experiments. Assuming the fine structure levels of atomic oxygen to be in local thermodynamic equilibrium (LTE), *Sharma et al.* [1988] showed that the 63 μm and 145 μm transitions could be inverted in the 90–250 km altitude range. The simulated signal with noise incorporated was inverted in the 145 μm channel by *Zachor and Sharma* [1989] and in the 63 μm channel by *Sharma et al.* [1990]. Since the idea that the fine structure levels were in LTE was not generally accepted, the newly calculated cross sections for transitions between the fine structure levels during O-O impacts [*Zygelman et al.*, 1994a, 1994b] were used to demonstrate that these levels were always in LTE at least up to 350 km altitude [*Sharma et al.*, 1994].

[4] Atoms with half-filled or completely filled outer electronic orbit have only isotropic polarizability and therefore do not Raman shift the frequency of the incident radiation. Atoms with neither half-filled nor completely filled outer electronic orbit, on the other hand, possess both isotropic and anisotropic polarizabilities and therefore do Raman shift the frequency of the incident radiation. From these considerations, *Schlossberg* [1976] pointed out that the fluorine atoms might be detected by monitoring the Raman scattered radiation and estimated

that about 10^{16} atoms could be detected by this method. The atomic oxygen ground electronic state (^{3}P) has eight electrons $1s^2 2s^2 2p^4$ and its outer electronic orbit is neither half-filled nor completely filled. It therefore has nonzero anisotropy of polarizability; hence Raman scatters incident radiation. *Dasch and Bechtel* [1981] measured, with an excitation source of 532.1 nm, the Raman scattering cross section without change in polarization of ground state atomic oxygen. These authors also calculated the Raman scattering cross section assuming that the ^{3}S$_1$ electronic state located at 76,700 cm^{-1} is the only state that makes a significant contribution to the Raman cross section. Since *Dasch and Bechtel* [1981] do not give details of their calculation, and since the transition moment, derived by us in Appendix A, differs by a factor of 1.4 from that given by these authors, we repeat their calculation using the full power of the angular momentum algebra [*Zare*, 1987]. We obtain results that are in order-of-magnitude agreement with the available measurements.

[5] Section 2 gives the formulation of the equations; the results are computed and compared with the earlier measurement and calculation of Dasch and Bechtel in section 3. Section 4 states the possible application of these results to measuring the atomic oxygen density and temperature in the terrestrial thermosphere.

2. Formulation

[6] The transition probability for going from state a to state b with the absorption of a photon of frequency ω from the electromagnetic field and the emission of one of frequency

$$\omega_{ba} \equiv \frac{(E_b - E_a)}{\hbar}$$

in solid angle $d\Omega$ is given by Fermi's Golden Rule [*Kramers*, 1964]

$$P = \frac{2\pi}{\hbar^2} \int d\omega |\langle b|W(\omega, t)|a\rangle|^2 \delta(\omega_{ba} - \omega)\rho(\omega)d\Omega, \quad (1)$$

where $\rho(\omega)$ is the density of states per unit frequency interval. $W(\omega, t)$ is the interaction energy of the electromagnetic field of frequency ω, and a spinless particle of mass μ, momentum **p**, and charge e given by

$$W(\omega, t) = -\frac{e}{\mu c}(A.p) + \frac{e^2}{2\mu c^2}A^2 \quad (2)$$

$$A(\omega, t) = c\left(\frac{2\pi\hbar}{\omega}\right)^{\frac{1}{2}}\epsilon(\exp(-i(k.r - \omega t)) + \exp(i(k.r - \omega t))). \quad (3)$$

The electromagnetic field is normalized to contain one photon of frequency ω in unit volume and **e** is a unit (polarization) vector in the direction of the electric field perpendicular to the propagation vector **k** of the radiation. The density of states $\rho(\omega)$ of the electromagnetic field per

unit frequency interval per unit volume in solid angle $d\Omega$ is given by

$$\frac{d\rho(\omega)}{d\omega} = \frac{\omega^2}{(2\pi c)^3}d\Omega. \quad (4)$$

It is usual in the literature to incorporate an additional factor of two in equation (4), corresponding to the two independent polarization directions of the emitted photon. Since we calculate the scattering cross section for the two directions of polarization separately, our density of states will not have that additional factor of two.

[7] We make the dipole approximation and assume that the dimensions of the atoms and molecules we are dealing with are very short compared to the wavelength of the electromagnetic radiation and approximate exp(ik.r) term in equation (3) by unity. Using the relationship between the expectation values of the momentum and dipole operators

$$\frac{e}{\mu}\langle n|p|m\rangle = i\omega_{nm}\langle n|\mu|m\rangle, \quad (5)$$

where

$$\omega_{nm} = \left(\frac{E_n - E_m}{\hbar}\right)$$

is the transition frequency between levels n and m. We can now write the first-order matrix elements of the interaction operator W between states n and m

$$\langle n|W|m\rangle = -i\omega_{nm}\left(\frac{2\pi\hbar}{\omega}\right)^{\frac{1}{2}}\epsilon.\mu_{nm}e^{i\omega_{nm}t}(e^{i\omega t} + e^{-i\omega t}). \quad (6)$$

Raleigh and Raman scattering are second-order processes, i.e., in going from the initial state a to final state b the interaction operator acts twice. The second-order interaction operator consists of three terms: (1) An incident photon of frequency ω is absorbed and the particle (atom or molecule) undergoes a transition to virtual state $|v\rangle$ followed by the emission of a photon of frequency ω_s with the particle going to the final state $|f\rangle$. (2) A photon of frequency ω_s is emitted and the particle undergoes a transition to virtual state $|v\rangle$ followed by absorption of a photon of frequency ω with the particle going to the final state $|f\rangle$. (3) A photon of frequency ω is simultaneously emitted and absorbed and the particle stays in the initial state.

[8] The first two terms are called the Kramers-Heisenberg terms while the third one is called the Waller term [*Mizushima*, 1970]. The Waller term is also called the A^2 term because it arises due to this interaction in the perturbation potential (equation (2)). An interesting point deserves mention here: The atom acts purely as a spectator in the Waller or the A^2 term, i.e., undergoing no change at all. This term, although 4–5 orders of magnitude smaller [*Loudon*, 1983], is still needed to obtain the commonly given expression for Rayleigh and Raman scattering given below (equation (7)).

[9] The three terms summed together give the differential cross section for scattering photons [*Mizushima*, 1970; *Kramers*, 1964; *Sharma and Levin*, 1973]:

$$\frac{d\sigma}{d\Omega} = \frac{\omega\omega_s^3}{c^4} \left| \sum_v \left(\frac{\langle f|(\varepsilon_s.\mu)|v\rangle\langle v|\varepsilon.\mu|i\rangle}{(E_v - E_i - \hbar\omega)} + \frac{\langle f|(\varepsilon.\mu)|v\rangle\langle v|\varepsilon_s.\mu|i\rangle}{(E_v - E_f + \hbar\omega)} \right) \right|^2 \tag{7}$$

where

$\hbar\omega$ is the energy of the incident photon

$\hbar\omega_s$ is the energy of the scattered photon

$|i\rangle$ is the wavefunction of the initial state of the particle

$|v\rangle$ is the wavefunction of the virtual state of the particle

$|f\rangle$ is the wavefunction of the final state of the particle

μ is the dipole moment operator

ε is the polarization (electric) vector of the incident photon

ε_s is the polarization (electric) vector of the scattered photon.

[10] We now write [*Zare*, 1987]

$$\varepsilon.\mu = \sum_{M=-1}^{1} \varepsilon_M^* \mu_M, \tag{8}$$

where μ_0 (ε_0), μ_{-1} (ε_{-1}), μ_1 (ε_1) are the projections of the vector μ (ε) on the unit vectors along the z, $(1/2)^{1/2}(x - iy)$, and $-(1/2)^{1/2}(x + iy)$ axes, respectively. The projection $\varepsilon_1(\varepsilon_{-1})$ corresponds to left (right) circular polarization. Radiation polarized along x-axis is obtained by the coherent (summing before taking absolute square) combination $(1/2)^{1/2}(\varepsilon_{-1} - \varepsilon_1)$ while that polarized along y-axis is represented coherently by the combination $(i/(2)^{1/2})(\varepsilon_{-1} + \varepsilon_1)$. Recalling that $\mu_m = (4\pi/3)^{1/2} \mu Y_{1m}(\Omega_\mu)$ we can write

$$\varepsilon.\mu = \left(\frac{4\pi}{3}\right)^{\frac{1}{2}} \mu \sum_{M=-1}^{M=+1} \varepsilon_M^* Y_{1M}(\Omega_\mu) \tag{9}$$

Similarly, we can write

$$\varepsilon_s.\mu = \left(\frac{4\pi}{3}\right)^{\frac{1}{2}} \mu \sum_{m=-1}^{m=+1} \varepsilon_{sm} Y_{1m}^*(\Omega_\mu). \tag{10}$$

To derive the scattering angle and polarization dependence of the emitted radiation, we follow *Sharma and Levin* [1973] and consider two coordinate systems: one fixed in the incident beam (coordinate system 1) and the other fixed in the scattered beam (coordinate system 2). We take the y-axes of the two beams along their respective directions of propagation. The z-axis of the two coordinate systems is taken perpendicular to the plane containing the incident and scattered beams. The two coordinate systems thus have the same z-axis and, in the experimental setup of *Dasch and Bechtel* [1981], coordinate system 1 can be transformed into coordinate system 2 by a 90° counter clockwise rotation about this axis. Further, the incident beam is polarized along the z-axis. Thus we are restricted to M in Equation 9 to only one value, M = 0. Further, without loss of generality, we can pick our space-fixed coordinate system to be coincident with the coordinate system 2.

[11] The ground state of atomic oxygen is ^3P_j, j = 1, 2, and 3. The different j levels are split because of the spin-orbit interaction with $^3P_2$ being the lowest at 0 cm^{-1}, $^3P_1$ at 158.2687 cm^{-1}, and $^3P_0$ at 226.9851 cm^{-1} [*Zink et al.*, 1991]. Using the Wigner-Eckart theorem, the matrix element of $\varepsilon.\mu$ between the initial and virtual states can be written [*Zare*, 1987]

$$\langle n''\ell''s''j''m''|\varepsilon.\mu|n\ell sjm\rangle = \left(\frac{4\pi}{3}\right)^{\frac{1}{2}} \langle n''\ell''|\mu|n\ell\rangle(-1)^{s+1-\ell-\ell''}\delta_{ss''}$$
$$\times [(2\ell''+1)(2j+1)]^{\frac{1}{2}}W(\ell j\ell''j'';s1)$$
$$\times (\ell'' \| Y_1 \| \ell)C(j\ell j'';m,0,m)\delta_{mm''} \tag{11}$$

and the matrix element in the uncoupled representation

$$(\ell'' \| Y_1 \| \ell) \equiv C(\ell 1\ell'';000)\left[\frac{3(2\ell+1)}{4\pi(2\ell''+1)}\right]^{\frac{1}{2}}, \tag{12}$$

giving

$$\langle n''\ell''s''j''m''|\varepsilon.\mu|n\ell sjm\rangle = \langle n''\ell''|\mu|n\ell\rangle C(\ell 1\ell'';00)(-)^{s+1-\ell-\ell''}\delta_{ss''}$$
$$\times [(2\ell+1)(2j+1)]^{\frac{1}{2}}W(\ell j\ell''j'';s\ell)$$
$$\times C(j1j'';m,0,m)\delta_{mm''} \tag{13},$$

where $\langle n''\ell''|\mu|n\ell\rangle$ is the radial matrix element of the dipole moment μ, C are the Clebsch-Gordan coefficients, and W is the Racah coefficient. The third "magnetic or M" quantum number in a Clebsch-Gordan coefficient is equal to the sum of the first two and is omitted when there is no danger of confusion. The matrix element of $\varepsilon_s.\mu$ between the virtual and final states can be similarly written as

$$\langle n'\ell's'j'm'|\varepsilon_s.\mu|n''\ell''s''j''m''\rangle = \langle n'\ell'|\mu|n''\ell''\rangle \sum_q (-)^q c_q \varepsilon_q$$
$$\times C(j''\ell j';m'',-q,m''-q)$$
$$\times (-\ell)^{s''+1-\ell'-\ell''}\delta_{s's''}[(2\ell''+1)$$
$$\times (2j''+1)]^{\frac{1}{2}}W(\ell''j''\ell'j';s''\ell)$$
$$\times C(\ell''1\ell';00) \tag{14},$$

where ε_q is a unit vector along the spherical axis and c_q is the projection of the unit vector along the polarization direction of the scattered beam in the coordinate system number 2, the space-fixed coordinate system.

[12] Using the relations

$$C(j1j'';m,0,m)C(j''1j';m,-q,m-q)$$
$$= \sum_f [(2j''+1)(2f+1)]^{\frac{1}{2}}W(j1j'1;j''f)$$
$$\times C(11f;0,-q,-q)C(jfj';m,-q,m-q) \tag{15}$$

and

$$C(jfj';m,-q,m-q) = (-1)^{j-m}\left(\frac{2j'+1}{2f+1}\right)^{\frac{1}{2}}C(jj'f;m,-m+q,q) \tag{16}$$

we can write

$$\langle f|(\varepsilon_s \cdot \mu)|v\rangle\langle v|\varepsilon_i \cdot \mu|i\rangle = \langle n'\ell'|\mu|n''\ell''\rangle\langle n''\ell''|\mu|n\ell\rangle\delta_{ss''}\delta_{s's''}$$

$$\times (-1)^{s+s''-\ell'-2\ell''-\ell''+j-m}\left[(2j+1)(2j''+1)^2\right.$$

$$\times (2j'+1)(2\ell''+1)(2\ell+1)\Big]^{\frac{1}{2}}C(\ell 1\ell'';000)$$

$$\times C(\ell''1\ell';000)W(\ell j\ell''j'';s1)W(\ell''j''\ell'j';s''1)$$

$$\times \sum_q (-)^q c_q \varepsilon_q \sum_f C(jj'f;m,-m+q,q)$$

$$\times C(11f;0,-q,-q)W(j1j'1;j''f) \qquad (17)$$

Averaging over the initial magnetic quantum numbers m and summing over the final ones for a given value of q we get

$$\frac{d\sigma}{d\Omega}(j\to j') = \frac{\omega\omega_s^3}{c^4}\sum_{f,q}(2j'+1)C^2(11f;0,-q,-q)|c_q|^2$$

$$\times\left|\begin{array}{l}\sum_v\left(\dfrac{1}{(E_v-E_i-\hbar\omega)}+\dfrac{1}{(E_v-E_f+\hbar\omega)}\right)\\[2mm]\times\langle n'\ell'|\mu|n''\ell''\rangle\times\langle n''\ell''|\mu|n\ell\rangle\\[2mm]\times(-1)^{2s-\ell-2\ell''-\ell'}\Big[(2j''+1)^2(2\ell''+1)(2\ell+1)\Big]^{\frac{1}{2}}\delta_{s's}\delta_{s'''s}\\[2mm]\times C(\ell1\ell'';000)C(\ell''1\ell';000)\\[2mm]\times W(\ell j\ell''j'';s1)W(\ell''j''\ell'j';s''1)W(j1j'1;j''f)\end{array}\right|^2$$

$$(18)$$

In equation (18) f denotes the rank of the polarizability tensor and q denotes the direction of the polarization vector of the scattered photon.

3. Computation of Raman Scattering Cross Sections

[13] Equation (18) is used to calculate Raman Scattering cross sections between the multiplet components of atomic oxygen with different j values. The Kronecker deltas require that the virtual states must also be spin triplets. Also, $\ell = \ell' = s = s' = 1$. For the Racah coefficient $W(j1j'1;j''f)$ with $j \neq j'$ to be nonzero, the index f must be nonzero. Therefore only anisotropic components of the polarizability tensor can Raman scatter between the multiplets of the ground state of atomic oxygen. Following *Dasch and Bechtel* [1981], we assume that only one virtual state, the $^3S_1$ state (76700 cm^{-1}), makes a significant contribution to the scattering process. Noting that $\ell'' = 0$ and $j'' = 1$ gives $W(1j01;11) = W(011j';11) = 1/3$. We also note that $\ell = \ell' = 1$, giving $C(110;00) = -(1/3)^{1/2}$ and $C(011;00) = 1$. Substituting these values as well as the dipole moments from Appendix A, we get

$$\frac{d\sigma}{d\Omega}(j\to j') = \frac{\omega\omega_s^3}{c^4}\frac{(1.2\times10^{-18})^4}{9}\sum_{f,q}(2j'+1)C^2(11f;0,-q,-q)$$

$$\times|c_q|^2\times\left|\left(\frac{1}{(E_v-E_i-\hbar\omega)}+\frac{1}{(E_v-E_f+\hbar\omega)}\right)\right.$$

$$\times W(j1j'1;1f)\Big|^2. \qquad (19)$$

If the scattered radiation has the same polarization as the incident beam, i.e., it is polarized in the z direction, then $q = 0$, $c_0 = 1$, and $f = 0, 2$. Since f has to be nonzero for transition from one multiplet level to another, only $f = 2$ is allowed. The combination $j = 1$, $j' = 0$, and $f = 2$ does not satisfy the triangular inequality leading to the Racah coefficient $W(1101;12) = 0$; thus the transition $^3P_1 \to {}^3P_0$, shifted 68.7165 cm^{-1} from the incident frequency, without change in the direction of the polarization vector is not Raman allowed. The differential cross section for Raman scattering from multiplet level j to level j' without change in the polarization is then

$$\frac{d\sigma}{d\Omega}(j\to j') = \frac{\omega\omega_s^3}{c^4}\frac{(1.2\times10^{-18})^4}{9}(2j'+1)C^2(112;0,0,0)$$

$$\times\left|\left(\frac{1}{(E_v-E_i-\hbar\omega)}+\frac{1}{(E_v-E_f+\hbar\omega)}\right)\right.$$

$$\times W(j1j'1;12)\Big|^2 \qquad (20)$$

For the incident radiation of 532.1 nm wavelength, the differential cross section for the $^3P_0 \to {}^3P_2$ Raman transition is 2.0×10^{-31} cm^2/str and that for the $^3P_1 \to {}^3P_2$ Raman transition is 1.5×10^{-31} cm^2/str; the ratio of the two cross sections is just the ratio of the squares of the Racah coefficients

$$\left(\frac{W(1121;12)}{W(0121;12)}\right)^2 = \frac{3}{4}.$$

The experimentally measured cross sections are $(4\pm1)\times10^{-31}$ and $(6\pm1)\times10^{-31}$ cm^2/str, respectively. The calculation of *Dasch and Bechtel* [1981] gives 1.2×10^{-31} cm^2/str for $^3P_0 \to {}^3P_2$ and 2.8×10^{-31} cm^2/str for $^3P_1 \to {}^3P_2$. The ratio R of the cross sections calculated by us $^3P_1 \to {}^3P_2/{}^3P_0 \to {}^3P_2 = 0.75$ while that obtained by Dash and Bechtel is 2.3; the experimental ratio being 1.5 ± 0.6.

[14] The expression for the differential cross section for Raman scattering with change in the direction of polarization is

$$\frac{d\sigma}{d\Omega}(j\to j') = \frac{\omega\omega_s^3}{c^4}\frac{(1.2\times10^{-18})^4}{9}\sum_{f=1,2}\sum_{q=-1,+1}(2j'+1)$$

$$\times C^2(11f;0,-q,-q)|c_q|^2$$

$$\times\left|\left(\frac{1}{(E_v-E_i-\hbar\omega)}+\frac{1}{(E_v-E_f+\hbar\omega)}\right)\right.$$

$$\times W(j1j'1;1f)\Big|^2 \qquad (21)$$

For the x direction of the polarization vector of the scattered photon, $q = \pm1$ and $|c_{-1}|^2 = |c_1|^2 = 1/2$. Using $C^2(111;0-1) = C^2(111;01) = C^2(112;0,-1) = C^2(112;01) = 1/2$, we can write the expression for the differential cross section as

$$\frac{d\sigma}{d\Omega}(j\to j') = \frac{\omega\omega_s^3}{c^4}\frac{(1.2\times10^{-18})^4}{9}\frac{1}{2}\times\sum_{f=1,2}(2j'+1)$$

$$\times\left|\left(\frac{1}{(E_v-E_i-\hbar\omega)}+\frac{1}{(E_v-E_f+\hbar\omega)}\right)\right.$$

$$\times W(j1j'1;1f)\Big|^2 \qquad (22)$$

Table 1a. Differential Cross Section (cm^2/str) Raman Scattering for 532.1 nm Radiation ($\times 10^{-31}$) Without Change of Polarization

Transition	Frequency Shift, cm^{-1}	Present Calculation	Dasch and Bechtel [1981] Calculation	Dasch and Bechtel [1981] Experiment
$^3P_0 \rightarrow {}^3P_2$	226.9851	2.0	1.2	4 ± 1
$^3P_1 \rightarrow {}^3P_2$	158.2686	1.5	2.8	6 ± 1
$^3P_0 \rightarrow {}^3P_1$	68.7165	0.0	0.0	<1

The f = 1 term gives zero for the differential cross section of the $^3P_0 \rightarrow {}^3P_2$ transition, since W(0121;11) = 0. The differential cross section of the $^3P_0 \rightarrow {}^3P_1$ Raman transition, which is zero when the polarization is unchanged, is 1.5×10^{-31} cm^2/str. The cross section for the $^3P_1 \rightarrow {}^3P_2$ transition is 0.6×10^{-31} cm^2/str.

[15] The f = 2 term gives zero for the differential cross section of the $^3P_0 \rightarrow {}^3P_1$ transition because W(0111;12) = 0. The cross sections with z to x change of polarization for the $^3P_1 \rightarrow {}^3P_2$ and $^3P_0 \rightarrow {}^3P_2$ transitions are 1.1×10^{-31} and 1.5×10^{-31} cm^2/str, respectively. The differential cross sections for Raman scattering with z to x change of polarization are 1.5×10^{-31}, 1.5×10^{-31}, and 1.7×10^{-31} cm^2/str for the $^3P_0 \rightarrow {}^3P_2$, $^3P_0 \rightarrow {}^3P_1$, and $^3P_1 \rightarrow {}^3P_2$ transitions, respectively. These results are summarized in Tables 1a and 1b.

4. Discussion

[16] We have calculated Raman scattering cross sections among the multiplet fine structure levels of atomic oxygen. We have shown that the isotropic component (tensor of rank zero) of the polarizability tensor makes no contribution to this cross section and have calculated the contributions of the polarizability tensors of rank one (vector) and two. This calculation, as well as that of *Dasch and Bechtel* [1981], gives order-of-magnitude agreement with the available experimental data. Considering the approximation of taking into account only one virtual state, this agreement cannot be considered unreasonable. The Raman LIDAR experiment proposed here would permit a three-dimensional map of each of the three fine structure components of the ground electronic state of atomic oxygen. Because these fine structure levels are in LTE up to at least 350 km altitude [*Sharma et al.*, 1994], a three-dimensional map of these levels would also give a three-dimensional map of the temperature.

Appendix A

[17] To evaluate the radial integral from the radiative lifetime of the $^3S_1 \rightarrow {}^3P_J$, J = 0,1,2, we start with Fermi's Golden rule

$$P = \tau^{-1} = \frac{2\pi}{\hbar^2} \int d\omega |\langle b|W(\omega,t)|a\rangle|^2 \delta(\omega_{ba} - \omega)\rho(\omega)d\Omega, \quad (A1)$$

where $\tau = 4.8$ ns [*Wiese et al.*, 1966] is the radiative lifetime of the $^3S_1 \rightarrow {}^3P_J$ transitions at 76,700 cm^{-1}, and the matrix element is the transion dipole moment between the upper and lower level. Proceeding as in section 2, we can write

$$P = \tau^{-1} = \frac{1}{2\pi\hbar}\left(\frac{\omega}{c}\right)^3 \int d\Omega |\varepsilon \cdot \langle b|\mu|a\rangle|^2, \quad (A2)$$

where we have written $\omega_{ba} \equiv \omega$ and ε is the polarization vector of the emitted photon and μ is the dipole moment operator. Anticipating that the absolute square of the matrix element will be shown to be angle independent, we integrate over the solid angle obtaining

$$P = \tau^{-1} = \frac{2}{\hbar}\left(\frac{\omega}{c}\right)^3 |\varepsilon \cdot \langle b|\mu|a\rangle|^2. \quad (A3)$$

Without loss of generality we take our space-fixed z-axis along the direction of propagation of the emitted photon. Using the Wigner-Eckart theorem, we obtain

$$\varepsilon \cdot \langle n'\ell's'j'm'|\mu|n\ell sjm\rangle = \left(\frac{4\pi}{3}\right)^{\frac{1}{2}}(-1)^{s-\ell-j}\delta_{ss'}[(2\ell'+1)(2j+1)]$$
$$\times W(\ell j\ell'j';s1)(n'\ell' \| Y_1 \| nl)\langle n'\ell'|\mu|n\ell\rangle$$
$$\times \sum_{M=-1,+1} \varepsilon_{-M}C(j1j';m,M,m') \quad (A4).$$

Using the relations

$$(n'\ell' \| Y_1 \| n\ell) = C(\ell 1\ell';00)\left[\frac{3(2\ell+1)}{4\pi(2\ell'+1)}\right]^{\frac{1}{2}} \quad (A5)$$

and

$$C(j1j';m,M,m+M) = (-1)^{j-m}\left(\frac{(2j'+1)}{3}\right)^{\frac{1}{2}}$$
$$\times C(jj'1;m,-m-M,-M), \quad (A6)$$

we get

$$\varepsilon \cdot \langle n'\ell's'j'm'|\mu|n\ell sjm\rangle = C(\ell 1\ell';000)\langle n'\ell'|\mu|n\ell\rangle(-)^{s-\ell-j'+j-m}\delta_{ss'}$$
$$\times \left[\frac{(2\ell+1)(2j+1)(2j'+1)}{3}\right]^{\frac{1}{2}}$$
$$\times W(\ell j\ell'j';s1)\sum_{M=-1,+1}\varepsilon_{-M}$$
$$\times C(jj'1;m,-m-M,-M). \quad (A7)$$

Taking the absolute square, averaging over the initial magnetic quantum number, and summing over the final ones and over M also, we get

$$|\varepsilon \cdot \langle \ell's'j'|\mu|\ell sj\rangle|^2 = C^2(\ell 1\ell';000)\left[\frac{2(2\ell+1)(2j'+1)}{3}\right]$$
$$\times W^2(\ell j\ell'j';s1)|\langle n'\ell'|\mu|n\ell\rangle|^2 \quad (A8)$$

Table 1b. Differential Cross Section (cm^2/str) Raman Scattering for 532.1 nm Radiation ($\times 10^{-31}$) With Change of Polarization

Transition	Frequency Shift, cm^{-1}	Present Calculation	Dasch and Bechtel [1981] Calculation	Experiment
$^3P_0 \rightarrow {}^3P_2$	226.9851	1.5	0.9	Not available
$^3P_1 \rightarrow {}^3P_2$	158.2686	1.7	1.4	Not available
$^3P_0 \rightarrow {}^3P_1$	68.7165	1.5	0.0	Not available

Recalling that the initial state is $^3S_1$, i.e., $s = 1$, $l = 0$, and $j = 1$, and final state is ^3P_j, i.e., $s' = 1$, $l' = 1$, and summing over $j' = 0, 1, 2$, ($C^2(011;00) = 1$ and $W^2(011j';11) = 1/9$), we get

$$|\varepsilon \cdot \langle n'|\mu|n\rangle|^2 = \frac{2}{27}\sum_{j'}(2j'+1)|\langle n'\ell'|\mu|n\ell\rangle|^2. \quad (A9)$$

Substituting in equation (A3), we get the equation for the radiative lifetime

$$P = \tau^{-1} = \frac{4}{27h}\left(\frac{\omega}{c}\right)^3\sum_{j'}(2j'+1)|\langle n'\ell'|\mu|n\ell\rangle|^2$$

$$= \frac{4}{3h}\left(\frac{\omega}{c}\right)^3\frac{\sum_{j'}(2j'+1)|\langle n'\ell'|\mu|n\ell\rangle|^2}{\sum_{j'}(2j'+1)} = \frac{4}{3h}\left(\frac{\omega}{c}\right)^3|\langle n'\ell'|\mu|n\ell\rangle|^2,$$

$$(A10)$$

giving $|\langle n'\ell'|\mu|n\ell\rangle| = 1.2 \times 10^{-18}$ esu-cm. *Dasch and Bechtel* [1981] obtain a value of 1.7×10^{-18} esu-cm for this matrix element, a value larger by factor of 1.4 than that calculated here.

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